Addressing Internal “Shuttle” Effect: Electrolyte Design and Cathode Morphology Evolution in Li-S Batteries

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Texas A&M University

June 9th, 2016

Project ID #: ES283

Overview

Timeline

- Start date: October 1, 2014
- End date: September 30, 2017
- Percent complete: 50%

Budget

- Total funding: $990,000
  - DOE share: $990,000
  - Contractor share: Personnel
- Funding received
  - FY15: $285,345
  - FY 16: $325,189

Barriers

- Barriers/targets addressed
  - Loss of available capacity
  - Materials evolution during cycling
  - Lifetime of the cell

Partners

- Interactions/ collaborations
  - Partha Mukherjee (TAMU Co-PI)
  - Vilas Pol (Purdue Univ., Co-PI)

- Project lead: TAMU

Relevance/Objectives

- **Objective:** Overcome Li-metal anode deterioration issues via protective passivation layers and minimizing polysulfide shuttle with advanced cathode structure design.
- **FY 2016 goals**: Understand Li_2S deposition reactions; influence of cathode mesostructure on strain accommodation; and SEI nucleation in presence of polysulfides with atomistic and mesoscopic modeling and coin cell testing.

- **Addressing targets and barriers**:
  - Controlled cathode mesoporous structures synthesized with a novel sonochemical method and new electrolyte formulations based on mesoscale and atomistic modeling efforts.
- **Impact:**
  - Alternative electrolyte chemistries and improved cathode architectures to deliver Li/S cells operating for 500 cycles at efficiency greater than 80%.

Relevance/Milestones

- a) Synthesis of C/S hybrid cathode materials and advanced characterization. (Dec. 14) **Completed**
- b) Determine structure and reactivity of PS/Li interface. (Mar. 15). **Completed.**
- c) Identification of reactions at the C/S cathode. (June 15). **Completed.**
- d) Analysis of cathode microstructure with mesoscopic model and experimental characterization. (Sept.15) **Completed (Go/No-Go)**
- e) Coin cell testing of C/S electrodes. (Dec.15) **Completed**
- f) Electrochemical and transport analysis of deposition and diffusion rates in composite cathodes- (Mar.16) **Completed**
- g) Influence of mesostructure on strain accommodation (June 16) (**Ongoing)**
- h) Reaction mechanisms and SEI formation at the Li anode in presence of PS species (Sep. 16) (**Ongoing) (Go/No-Go)**

Approach/Strategy

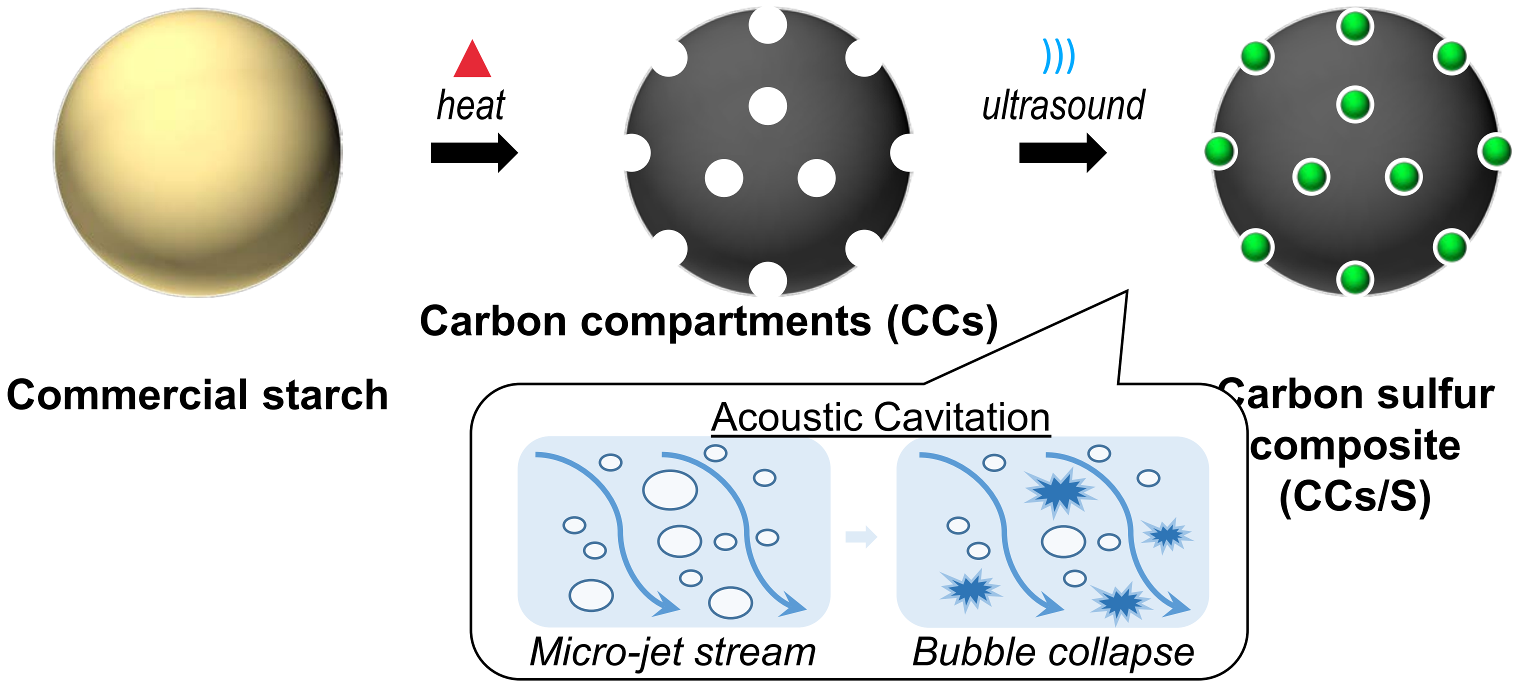
- **Overall Technical Approach/Strategy**:
  - A mesoscale model of electrode mesoporous structures based on stochastic reconstruction allows virtual screening of cathode microstructural features and effects on electronic/ionic conductivity and morphological evolution.
  - Interfacial reactions at the anode due to the presence of polysulfide species will be characterized with ab initio methods.
  - Data and detailed structural and energetic information from atomistic-level studies used in mesoscopic-level analysis of cathode interfacial reactions.
  - Novel sonochemical fabrication method for controlled cathode mesoporous structures and new electrolyte formulations based on mesoscale and atomistic modeling efforts.

- **Progress towards FY15 and FY16 milestones and Go/No Go decisions**: New understanding of interfacial anode chemistry and deposition reactions at the cathode. Analysis and test of materials for PS retention at the cathode.

Technical Accomplishments: Barriers Addressed

- **Complexity of Li metal reactivity**
  – *Characterized PS decomposition* at the Li metal anode and formation of a Li_2S film
- **Control of cathode microstructure**
  – *Novel sonochemical process* allows for low-cost and simple process for fabrication of effective C-S cathodes. Mesoscopic modeling reveals effects of microstructure on macroscopic properties
- **PS retention at cathode**
  – *Identified and tested specific materials* to retain soluble PS species at the cathode

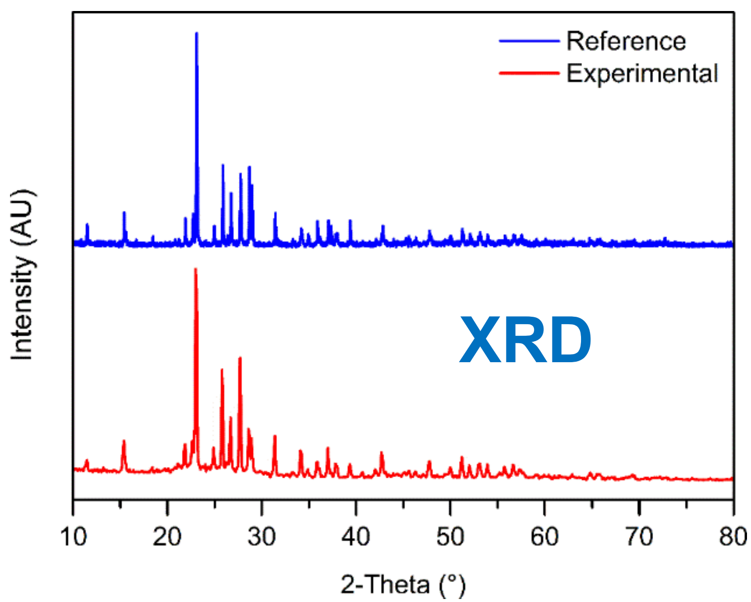
Technical Accomplishments
Carbon compartments/S composites

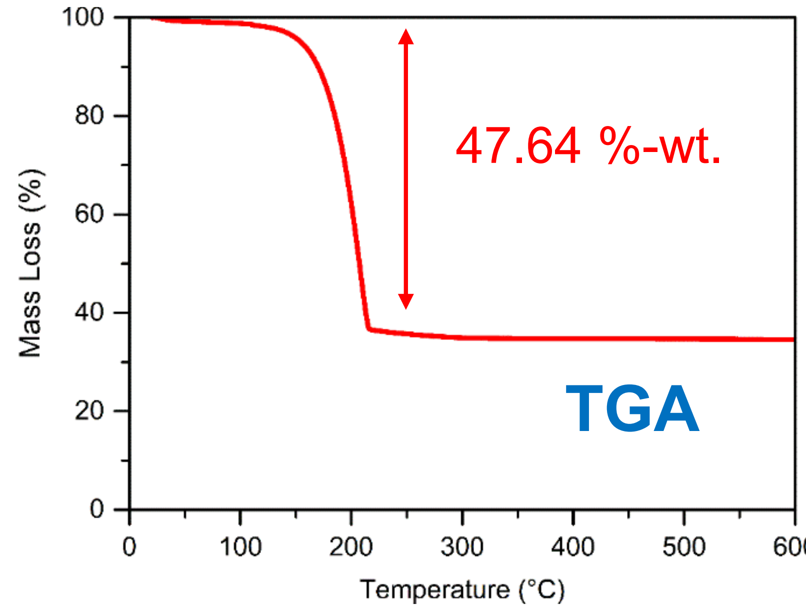


- Pyrolysis of starch produces a porous carbon substrate.
- Sonochemistry allows high T (5000 K), high P (1000 atm), rapid thermal rates (100K/s), and stream speeds (400 km/h) via acoustic cavitation.
- Sonochemical reduction of $Na_2S_2O_3$ to S in presence of dil $HCl_{(aq)}$

Milestone Q1/Y1: Lab scale C/S composite synthesized and characterized ✓

Technical Accomplishments
CC/S composites: characterization



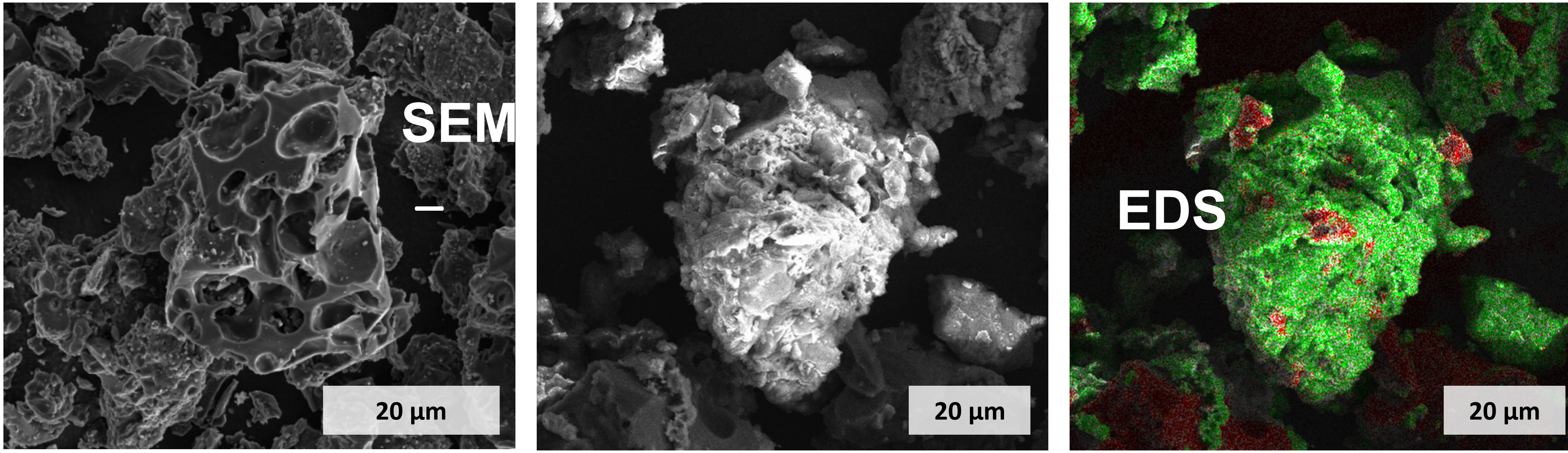


- Orthorhombic α-sulfur formed in the composite via sonochemical synthesis (from XRD analysis)

- 47.64 %-wt. sulfur loaded into the CC/S composite (from TGA analysis)

Milestone Q1/Y1: Lab scale C/S composite synthesized and characterized ✓

Technical Accomplishments
CC/S composites: SEM & mapping

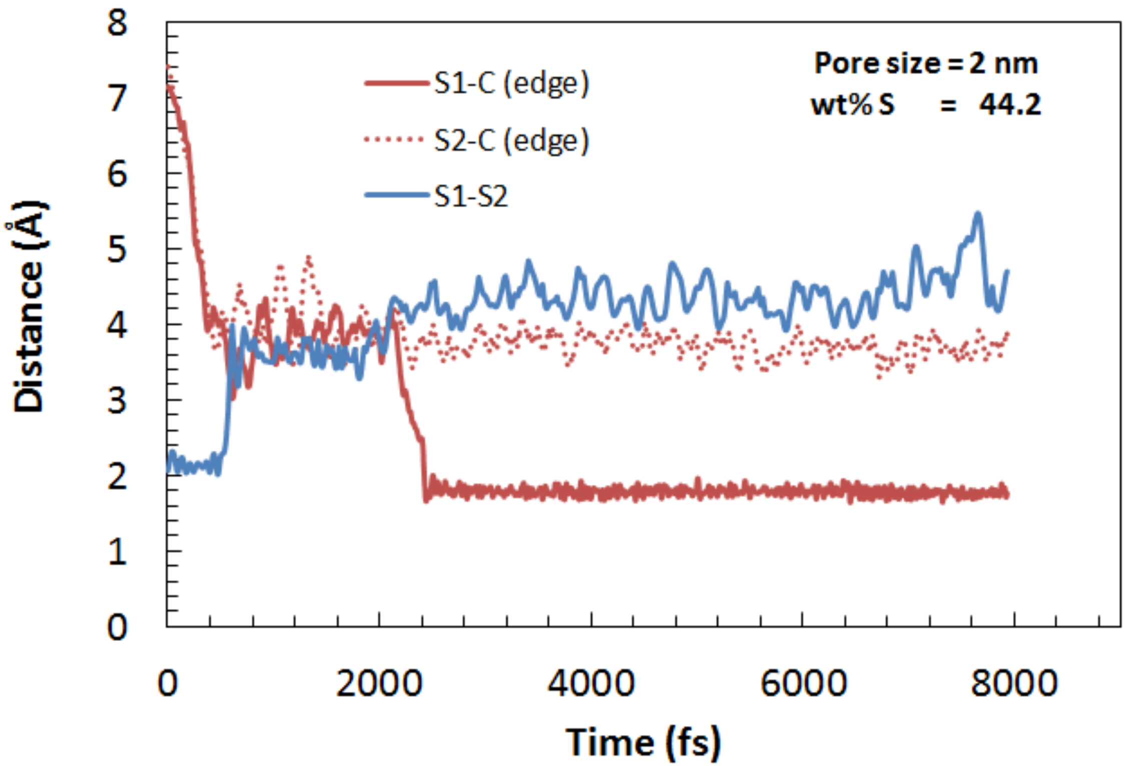


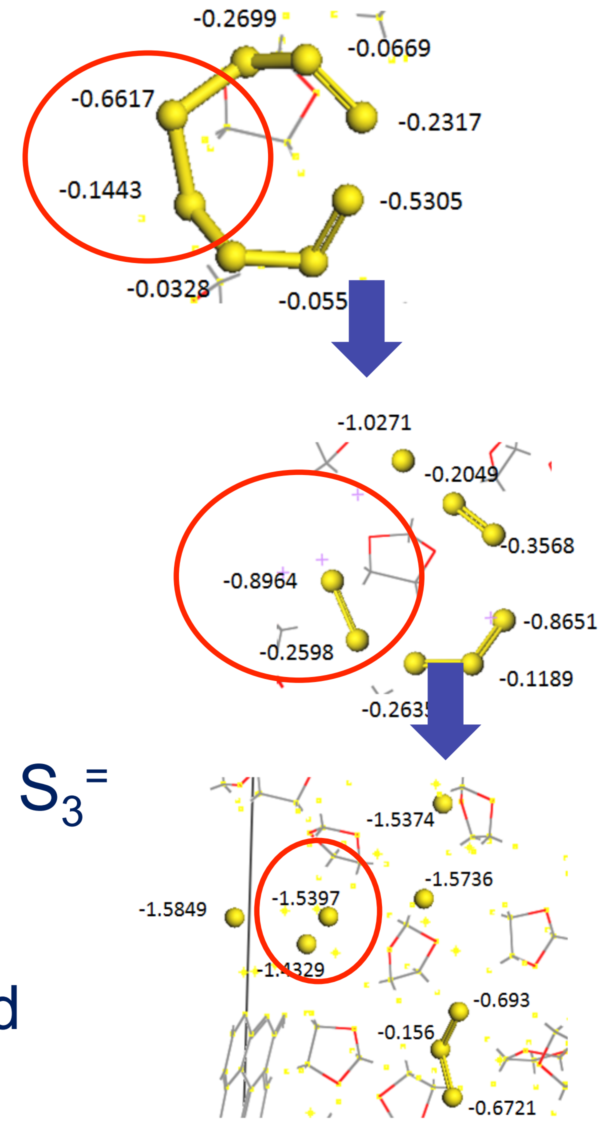
CC only | CC/S | Carbon & Sulfur

- Pyrolysis of commercial starch produces a bimodal-porous carbon with large micro-compartments and small pores
- Sonochemical procedure creates a thin layer of sulfur coating surface and inhabiting pores

Milestone Q1/Y1: Lab scale C/S composite synthesized and characterized

Technical Accomplishments:
Effects of Carbon at the C/S Cathode



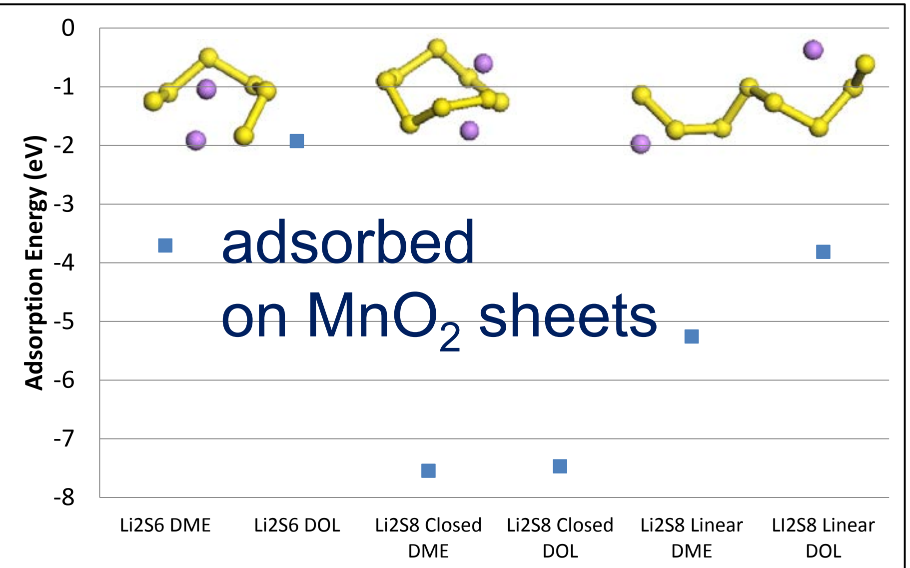


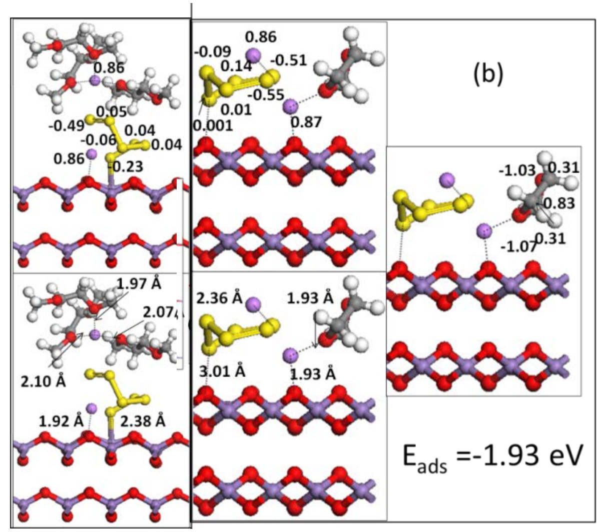
Fast reduction of S_8: Main products $S_2^=$ and $S_3^=$

$S_2^=$ is reduced and trapped at the C edge

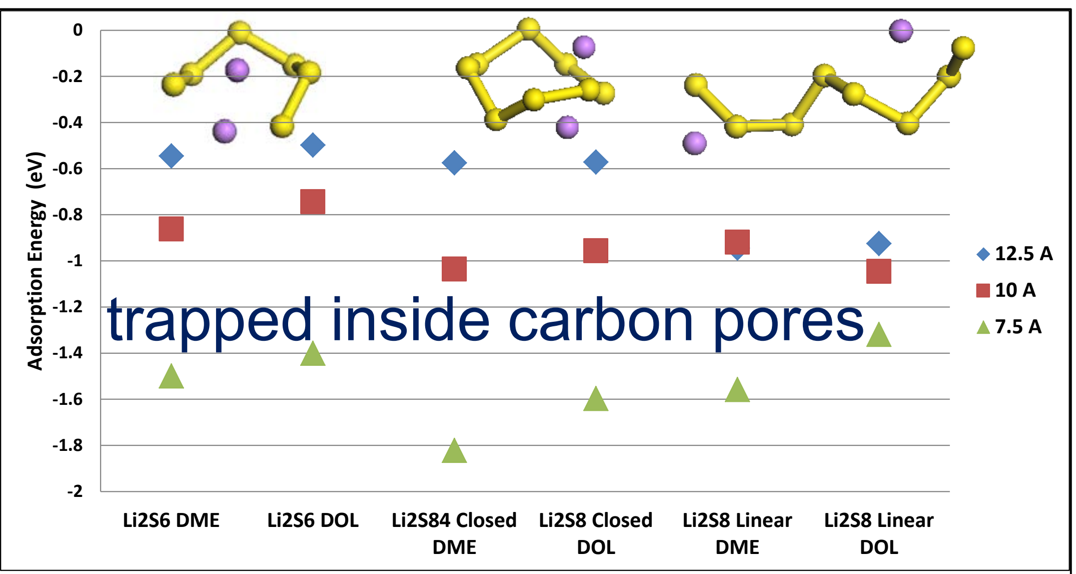
Milestone Q3/Y1: Dissolution, reduction, and lithiation of S at the C-S cathode

Technical Accomplishments: Soluble PS Retention at the Cathode Surface





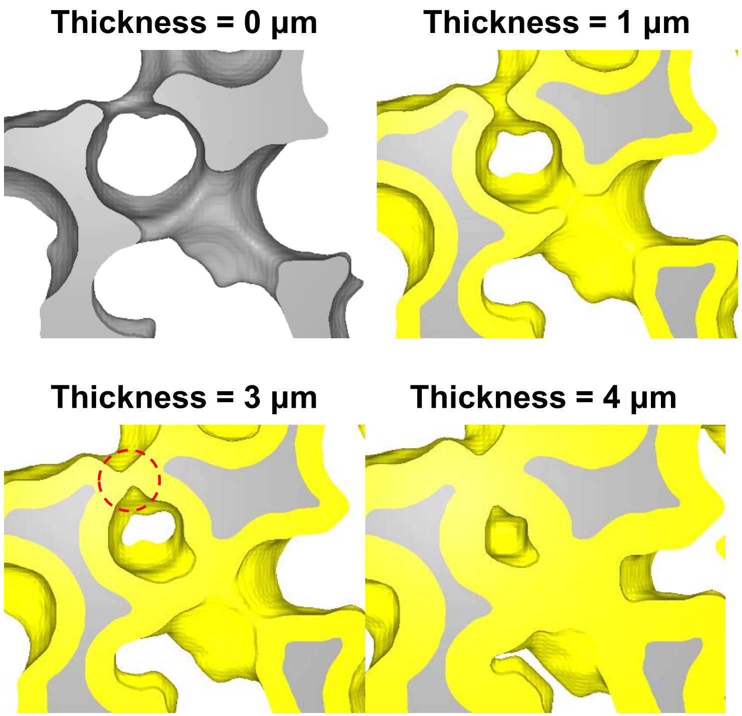
PS can form strong covalent bonds but no dissociation was found on the MnO_2 (001) plane in contrast to Fe_2O_3 surfaces

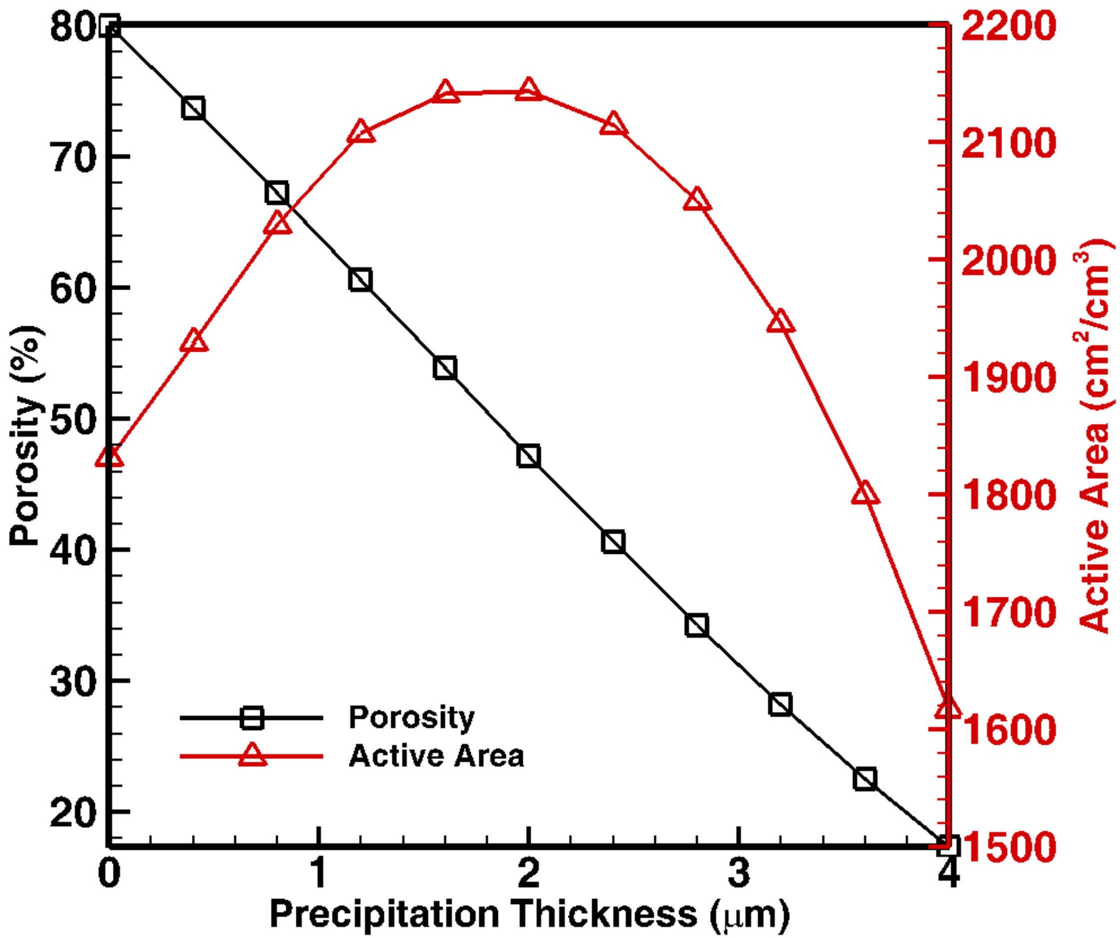


PS retention mechanisms have been identified

Milestone Q3/Y1: Dissolution, reduction, and lithiation of S at C-S cathode ✓

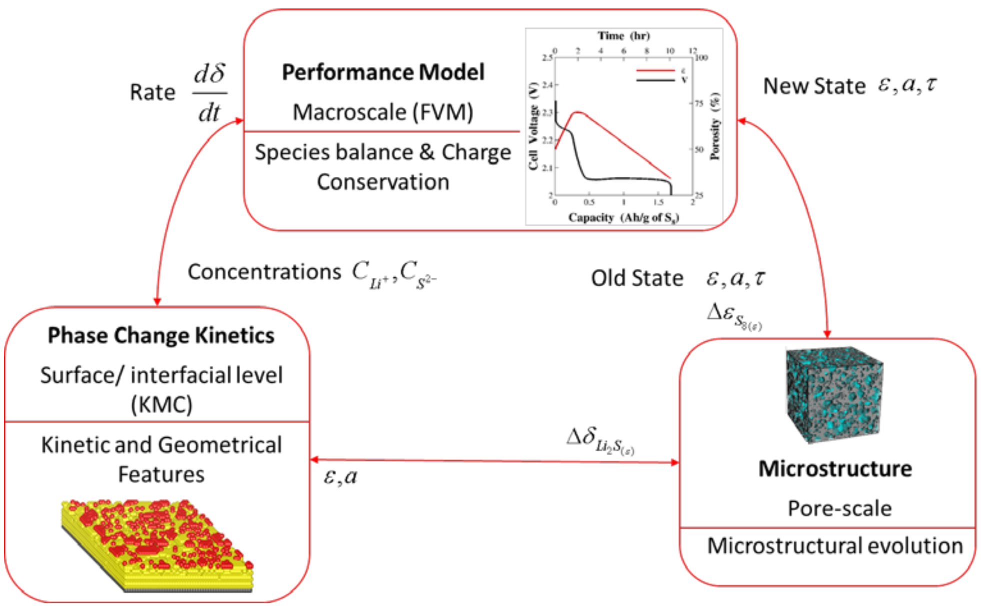
Technical Accomplishments: Microstructure variation due to deposition

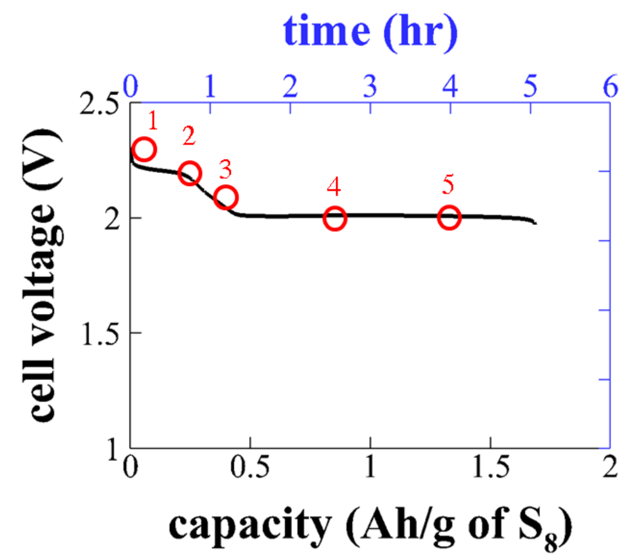


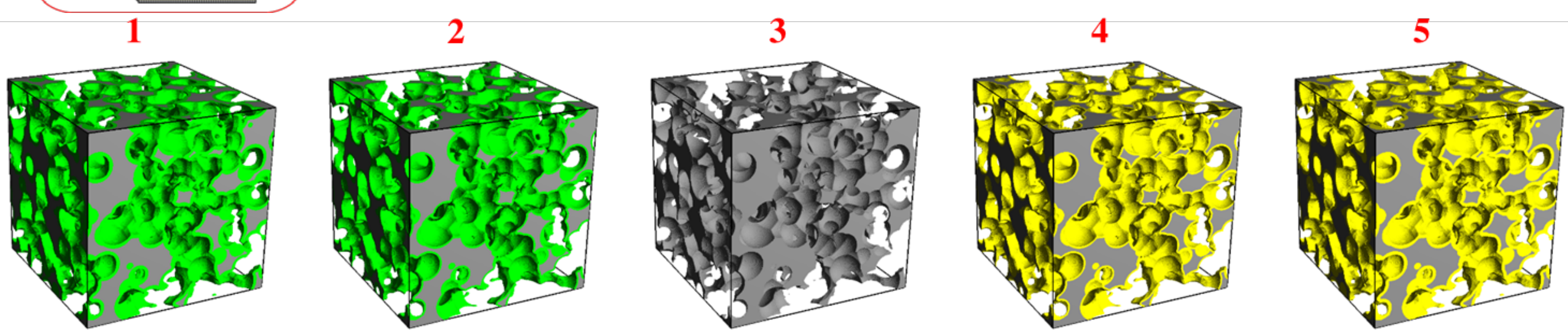


Milestone Q4/Y1: Elucidate cathode morphology evolution and microstructure transport interaction ✓

Technical Accomplishments:
Multiscale Modeling of Li-S Battery

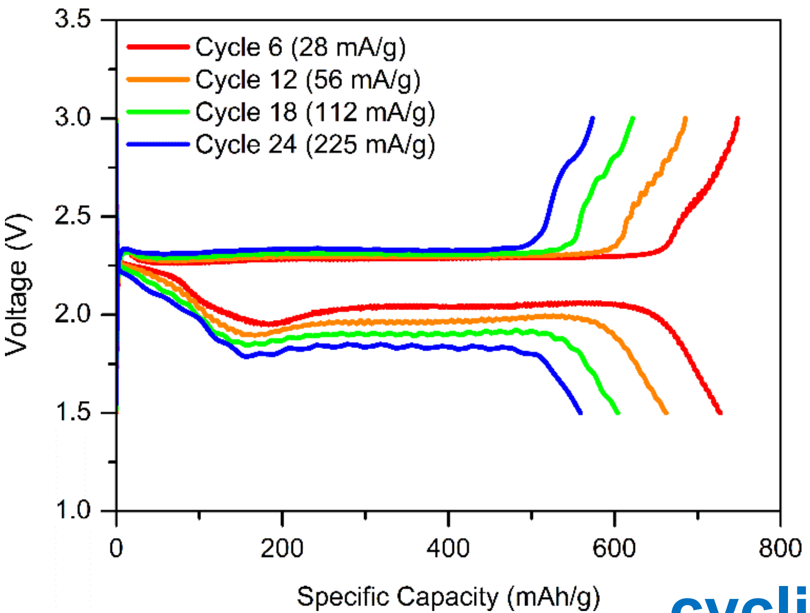


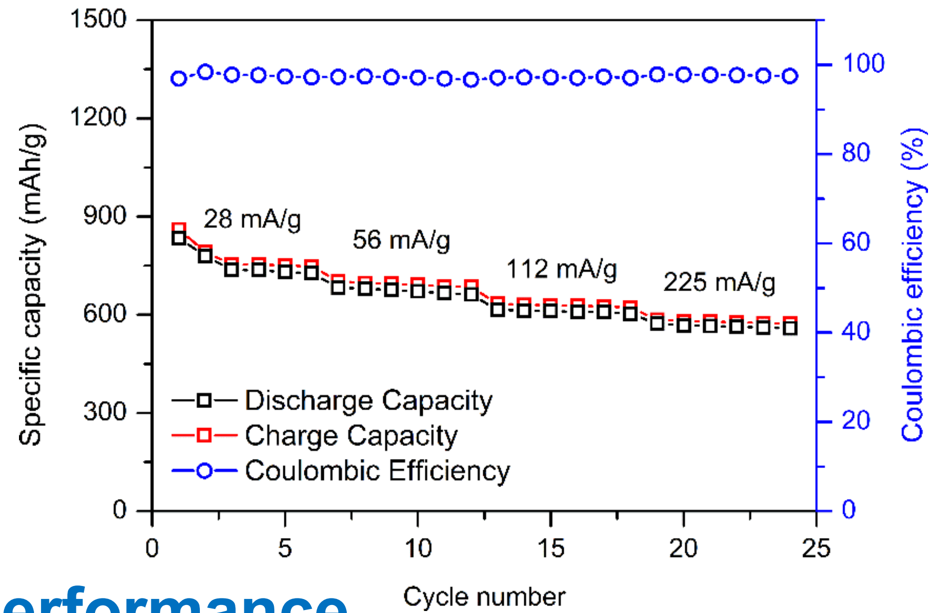




Milestone Q2/Y2: Gain an understanding of the mesoscopic reactions using electrochemical and transport modeling

Technical Accomplishments
CC/S composites: rate performance





cycling performance

- 750mAh/g capacity at 28 mA/g specific current.
- Electrolyte: DOL (50 %-vol.),1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (50 %-vol.), Li TFSI salt (1.0 M conc.)

Milestone Q1/Y2: Coin cell testing of C/S electrodes ✓

Technical Accomplishments:
Reactivity of Soluble PS at the Li Metal Anode

Long-chain Li_2S_8 polysulfide extremely reactive with lithium

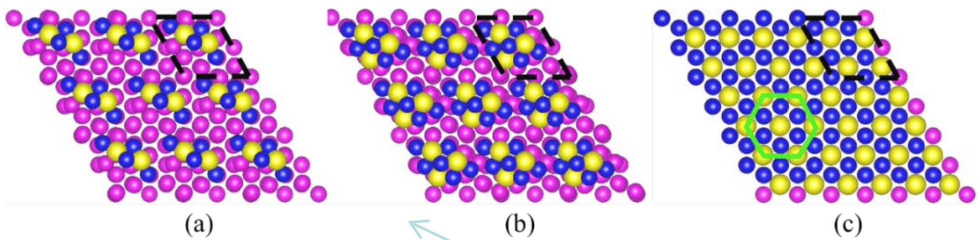
Possible reactions	Gas-Phase		EC Solvent		DOL Solvent	
	ΔE (0K)	ΔG(298K)	ΔE (0K)	ΔG(298K)	ΔE (0K)	ΔG(298K)
$Li_2S_8 + 2Li \rightarrow Li_2S + Li_2S_7$	**-3.56**	**-3.43**	**-5.53**	**-5.39**	**-5.18**	**-4.85**
$Li_2S_8 + 2Li \rightarrow Li_2S_2 + Li_2S_6$	-5.63	-5.38	-6.02	-5.92	-5.64	-5.51
$Li_2S_8 + 2Li \rightarrow Li_2S_3 + Li_2S_5$	-5.32	-5.17	-6.19	-6.09	-5.78	-5.65
$Li_2S_8 + 2Li \rightarrow 2Li_2S_4$	-6.95	-6.69	-6.28	-6.14	-6.15	-5.98

All reactions exothermic and ΔG <0 (spontaneous). Energies in eV

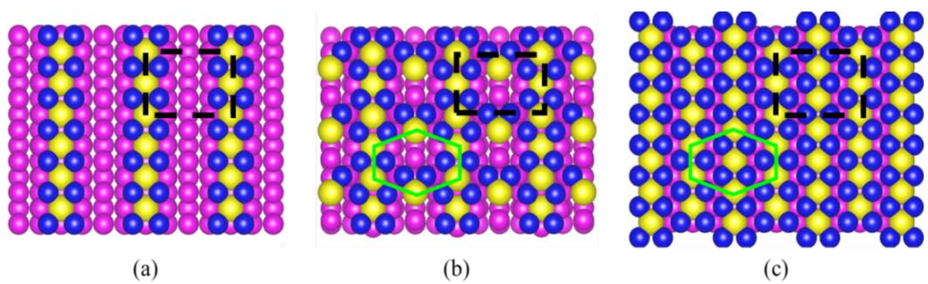
Milestone Q2/Y1: ✓ Nucleation and growth of PS deposits at Li metal surface

Technical Accomplishments: Nucleation and Growth of Li_2S at Li Surfaces

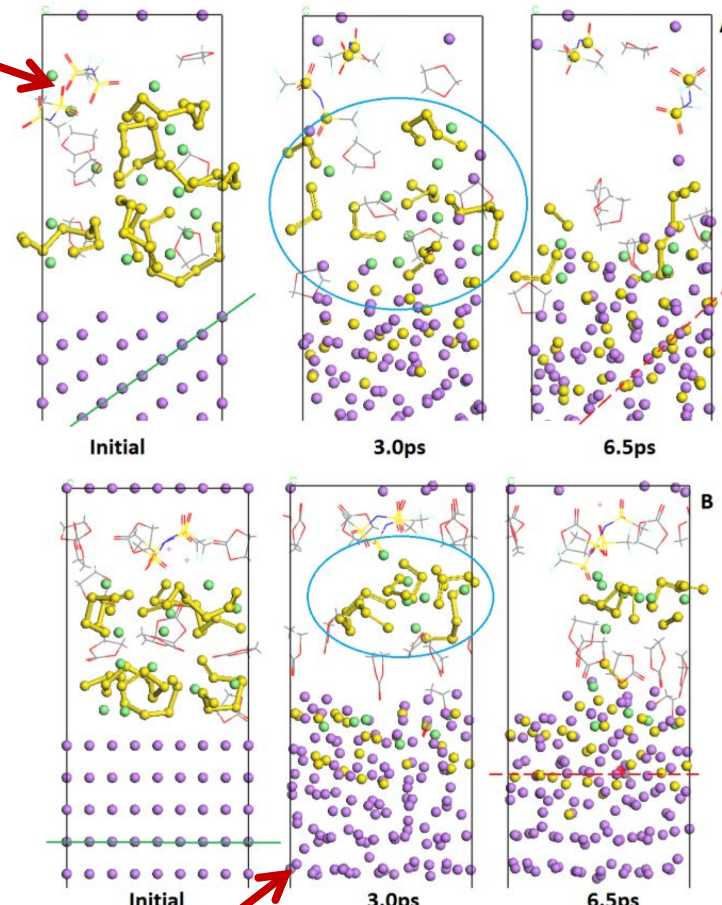
electrolyte solution: solvent + salt + PS



Li_2S molecular adsorption and PS decomposition on Li(111)



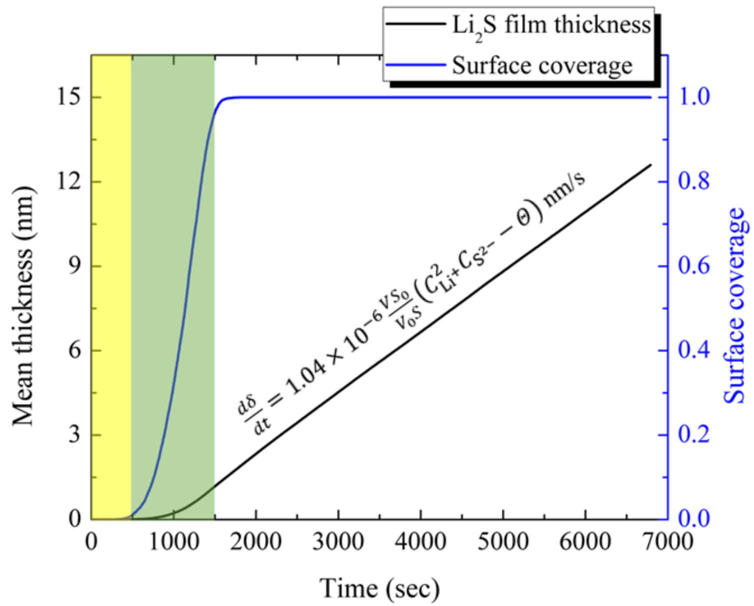
Li_2S molecular adsorption and PS decomposition on Li(110)



PS (yellow) extremely reactive; decomposes before salt or solvent

Milestone Q2/Y1:Thermodynamics and kinetics of nucleation and growth of PS deposits at the Li metal surface

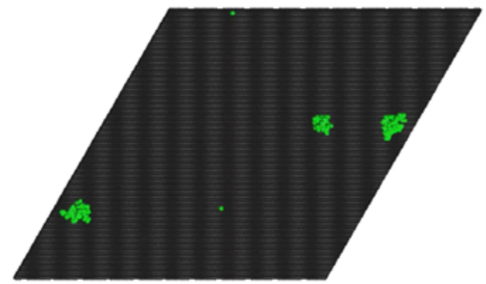
Technical Accomplishments:
Li_2S Film growth: Mesoscale modeling

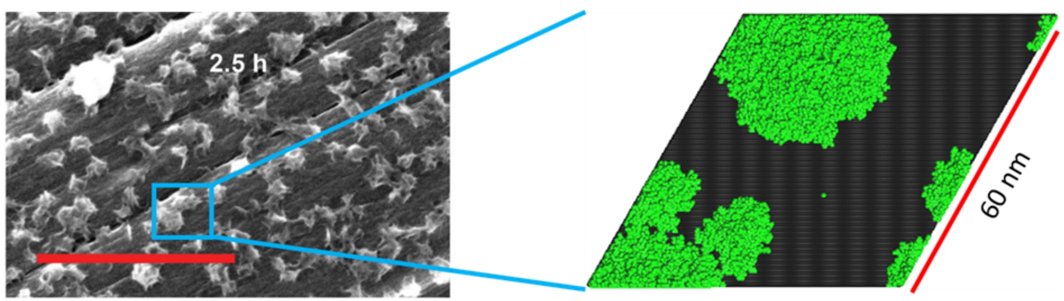


Competition between Li_2S adsorption and desorption

Li_2S islands formation and spread

Li_2S film growth





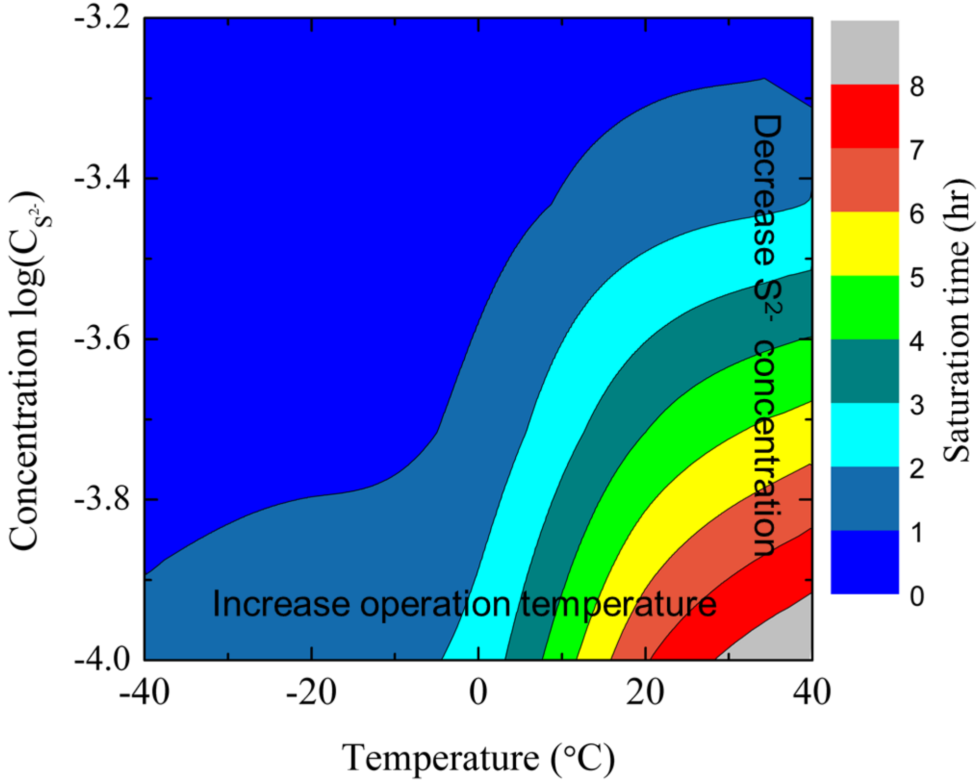
18% coverage

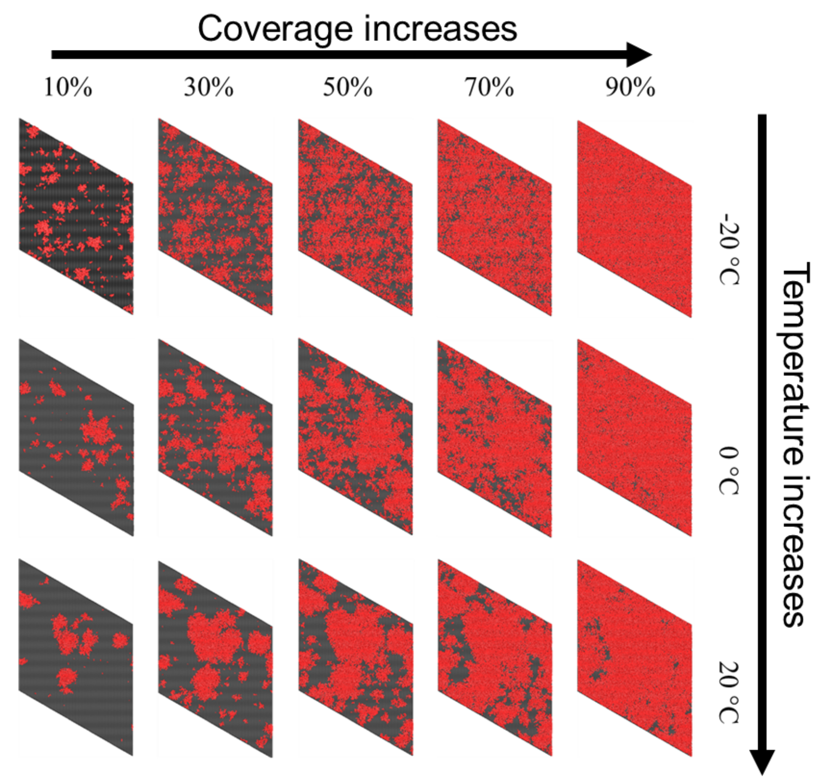
Fan et al., *Adv. Mater.* **27**(2015)5203

25% coverage

Milestone Q2/Y1: Characterization of thermodynamics of nucleation and growth of PS deposits on the Li surface ✓

Technical Accomplishments:
How to defer the surface passivation





Milestone Q2/Y1: Characterization of thermodynamics of nucleation and growth of PS deposits on the Li surface ✓

Responses to Previous Years Reviewers' Comments

This project started FY15;
it was not evaluated last year

Collaboration and Coordination with Other Institutions

- Purdue University: This project is a collaboration between Texas A&M University (Balbuena, Mukherjee) and Purdue University (Pol). The groups communicate via teleconference and site visits.
- Pacific Northwest National Laboratory (PNNL): The TAMU team interacts with the group of Dr. Jason Zhang regarding analysis of strategies to mitigate extreme Li metal reactivity. We are currently investigating the reasons for the apparent mitigation effects caused by high salt concentrations as a function of the nature of the salt.
- Argonne National Laboratory (ANL): Dr. Vilas Pol (Purdue) collaborates with the group of Dr. Jeffrey Elam and Dr. Anil Mane at ANL in the applications of ALD coatings for polysulfide capture at the cathode.

Remaining Challenges and Barriers

- Characterize **SEI reactions at the Li metal anode** and effects of higher salt concentration on such reactions.
- Evaluate influence of **mesostructure on strain accommodation** in the cathode.
- Identify **reasons for failures and successes of specific electrolyte compositions** and impact on Li anode behavior.
- Estimate the influence of cathode microstructure and electrolyte properties on **cathode performance**.
- **Scale up** of cathode composites.

Proposed Future Work

- **Rest of FY16**:
  - effects of deposition induced stress in cathode structure
  - mechanisms of SEI reactions at anode as functions of electrolyte composition
  - reasons for electrolyte failure and success
- **FY17:**
  - influence of cathode structure and electrolyte properties on cell performance
  - develop stable electrolytes
  - produce 3-5gr of C/S composite and achieve capacity > 800 mAh/g during at least 400 cycles

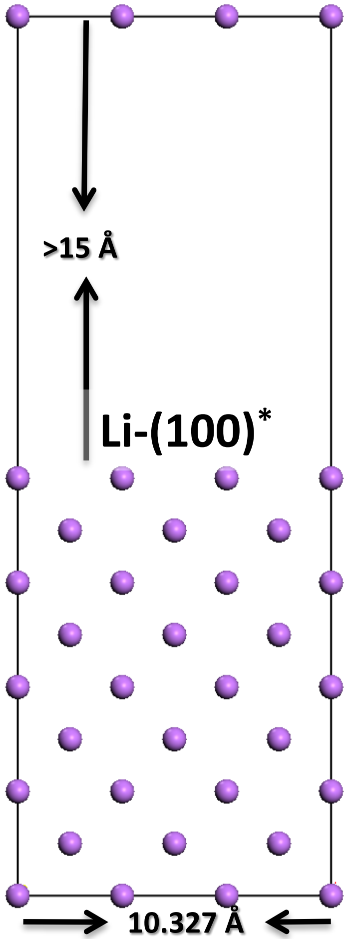
Summary Slide

- **Relevance:** Overcome Li-metal anode deterioration issues via protective passivation layers and minimizing polysulfide shuttle with advanced cathode structure design.
- **Approach:** Synthesis, characterization, and testing of a C/S composite cathode guided by multiscale modeling (atomistic and mesoscopic) focusing on electrolyte composition and cathode morphology effects on cell performance.
- **Technical Accomplishments:** Development of low-cost synthesis and characterization of a C/S composite cathode with promising performance; identification of effects of carbon on sulfur reductions; effects of microstructure variation due to deposition; elucidation of reactions of the polysulfides on the Li metal anode.
- **Collaborations:** Purdue University (Co-PI); evaluation of additives and salts (with PNNL); cathode coatings (with ANL).
- **Future Work:** Development of stable electrolytes; scale up cells and achieve target capacity; model effects of cathode microstructure on cell performance.

Technical Back-Up Slides

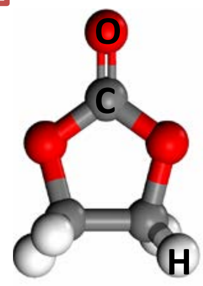
Methodology

DFT optimization: Anode Model and Electrolyte Species

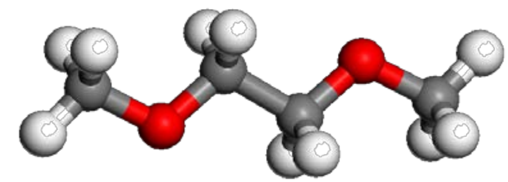


Anode Model

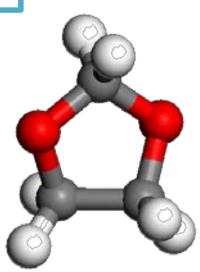
EC Ethylene carbonate



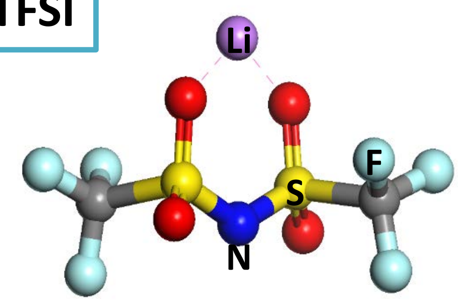
DME 1,2-Dimethoxyethane



DOL 1,3-dioxolane



LiTFSI



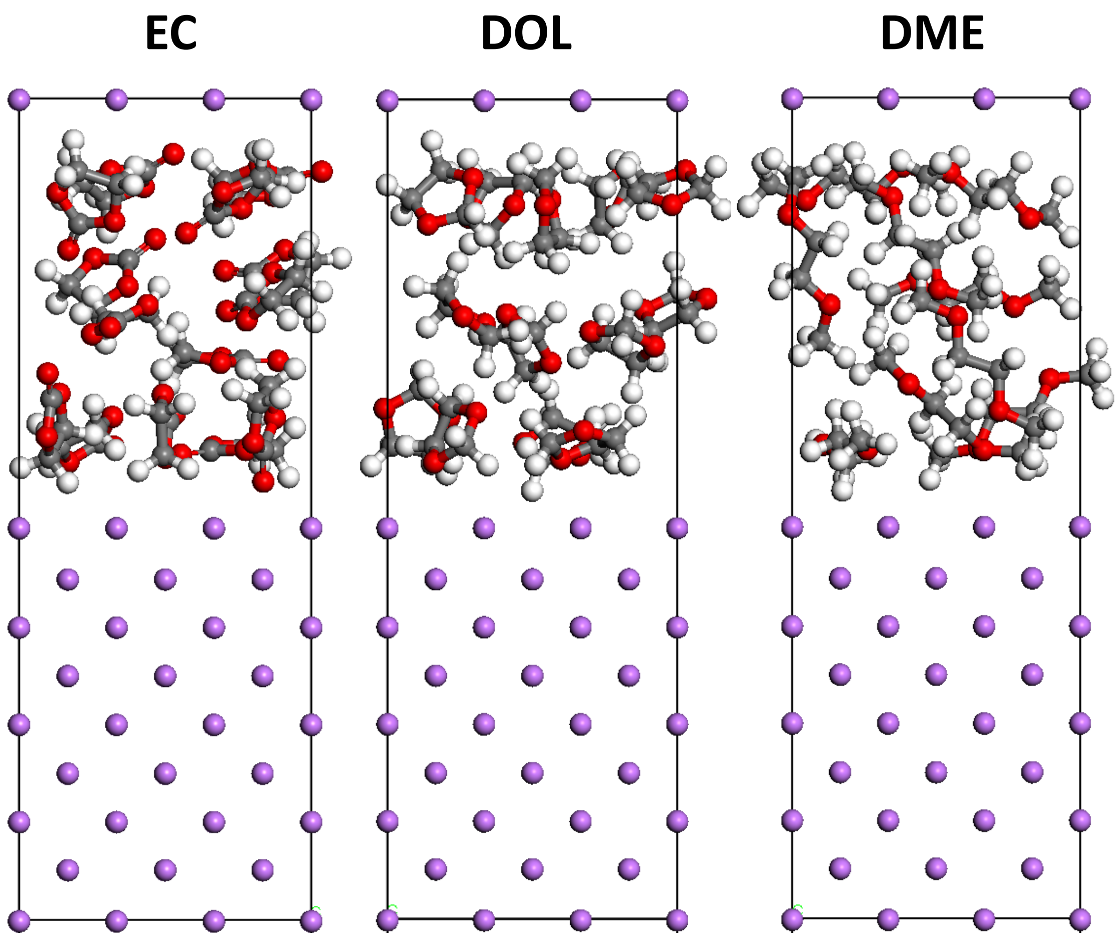
1 M concentration

- Optimizations performed using the Vienna ab initio simulation package **(VASP)**
- Perdew-Burke-Ernzerhof functional **(GGA-PBE)**
- Cutoff energy: **400 eV**
- **LiTFSI** (**G09**: B3PW91/6-311++G(p,d))

*Most stable facet

Methodology

Ab-initio MD simulations at 330 K (~20 ps)



$\rho = 1.32\ g/cm^3$ $\rho = 1.06\ g/cm^3$ $\rho = 0.87\ g/cm^3$

- *Ab-initio* MD performed using **VASP**
- **GGA-PBE** functional
- Cutoff energy: **400 eV**
- **2x2x1** k-points Monkhorst–Pack mesh sampling
- Timestep: **1 fs**
- **NVT ensamble**

(Pure Solvents)

Camacho-Forero , Smith, Bertolini, Balbuena, JPCC, 2015

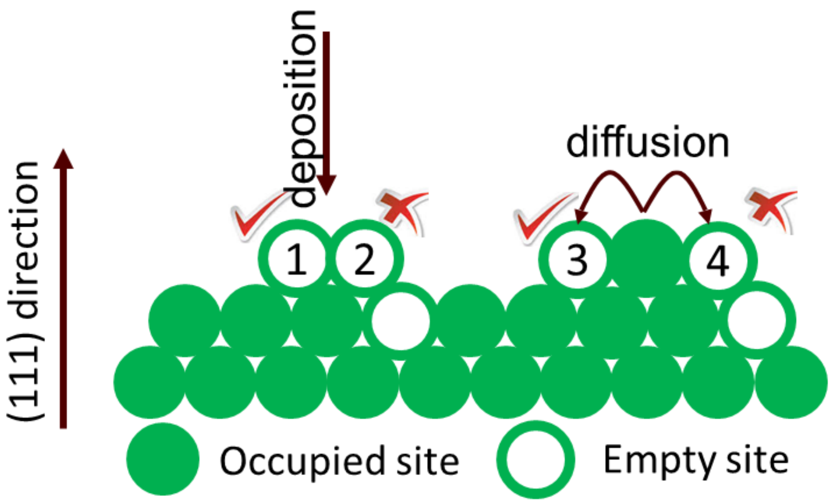
Li C O H

Li_2S Growth Model: Deposition + Diffusion

Coarse-Grained Kinetic Monte Carlo Method

- Only consider the insoluble Li_2S molecule deposition on crystal Li_2S (111) surface

- A coarse-grained model is developed to describe the structure of Li_2S (111) film.



k_0: reaction rate constant
N_A: Avogadro constant
V: Volume of electrolyte
S: solid-electrolyte interfacial area
S_a: area per Li_2S unit
C: reactant concentration
Θ: Li_2S solubility
ν: jump frequency
E_b: diffusion barrier
κ: Boltzmann constant
T: temperature

- The diffusion process is governed by

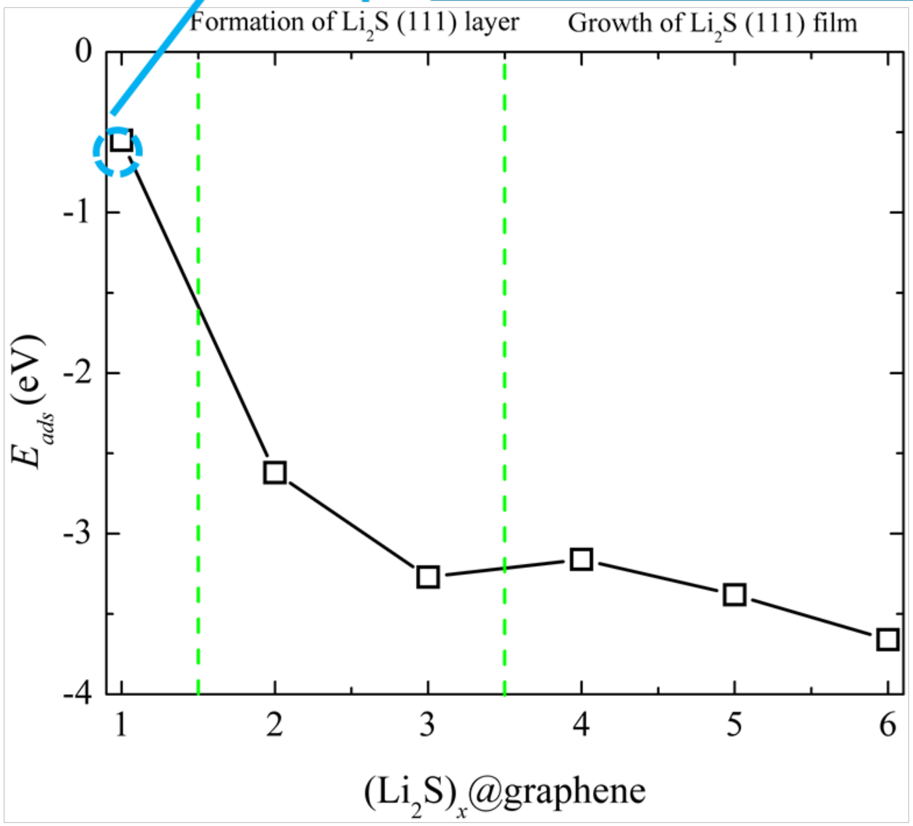
$$K_{dif} = \nu \cdot \exp(-\frac{E_b}{\kappa T})).$$

- The deposition process is governed by

$$K_{dep} = k_0 N_A V \frac{S_a}{S} \left(C_{Li^+}^2 C_{S^{2-}} - \Theta\right).$$

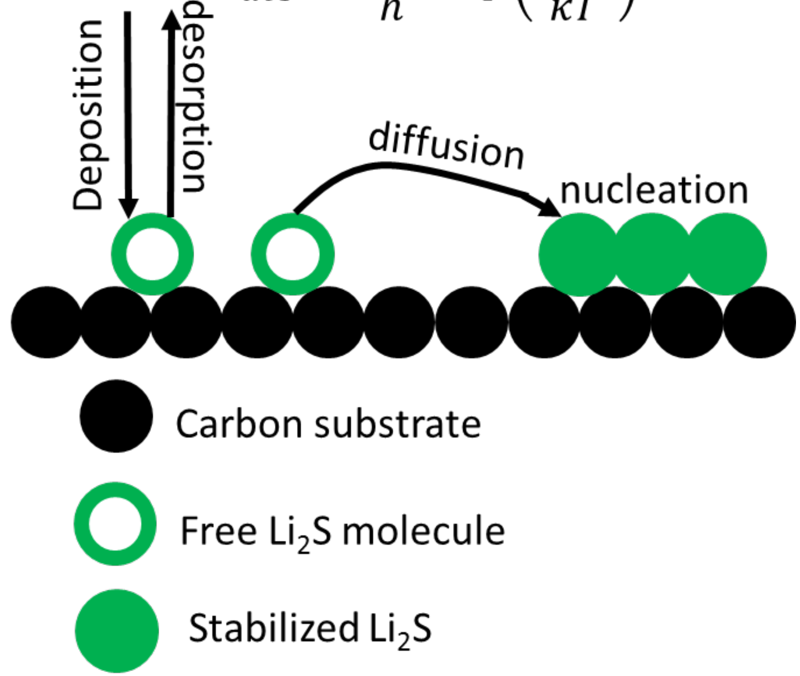
Li_2S Growth Model: Desorption

Li_2S desorption should be considered due to the relatively weak chemical interaction

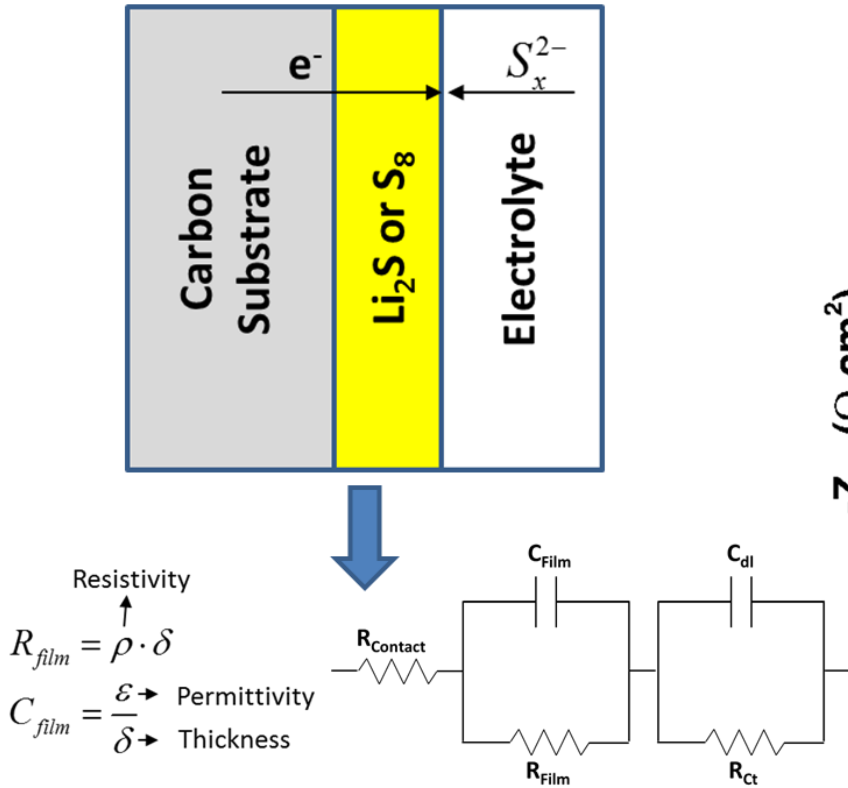


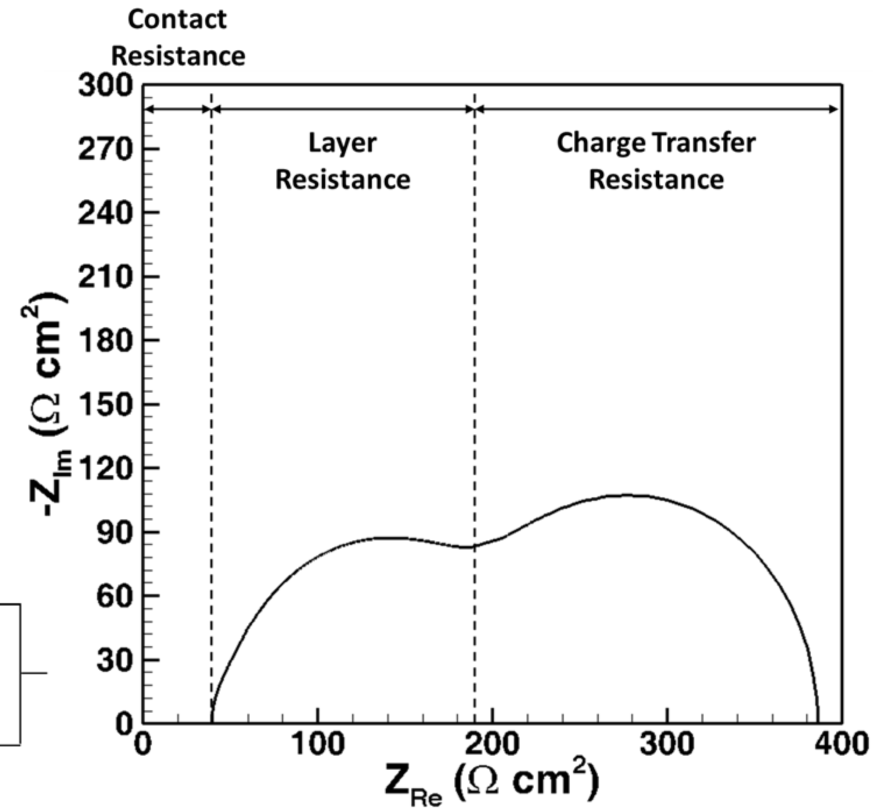
$$E_{ads} = \frac{1}{x}\left(E(G, xLi_2S) - E(G) - xE(Li_2S)\right)$$

$$R_{des} = \frac{2\pi T}{h}\exp\left(\frac{E_{ads}}{\kappa T}\right)$$



Impedance Response of Cathode of Li-S Battery





$R_{contact}$: Contact Resistance between carbon substrate and thin layer.
R_{Film}: Resistance from thin layer.
R_{Ct}: Charge transfer resistance from electrochemical reaction.
C_{Film}: Capacitance from thin layer.
C_{dl}: Capacitance from double layer.

Note: *Diffusion resistance is not included and discussed in this model.*

Cell Performance Prediction: Electrochemical Reactions

Anodic Reaction

$$Li \rightleftharpoons Li^{+} + e^{-}$$

Other reactions are electrochemical in nature

Cathodic Reactions

Chemical reactions

$$\boxed{S_{8(l)} \rightleftharpoons S_{8(s)}}$$

$$\frac{1}{2}S_8^{\,2-} \rightleftharpoons \frac{1}{2}S_{8(l)} + e^{-}$$

$$2S_6^{2-} \rightleftharpoons \frac{3}{2}S_8^{2-} + e^{-}$$

$$\frac{3}{2}S_4^{2-} \rightleftharpoons S_6^{2-} + e^{-}$$

$$S_2^{2-} \rightleftharpoons \frac{1}{2}S_4^{2-} + e^{-}$$

$$S^{2-} \rightleftharpoons \frac{1}{2}S_2^{2-} + e^{-}$$

$$\boxed{2Li^{+} + S^{2-} \rightleftharpoons Li_2S \downarrow}$$

Cell Performance Prediction: Governing Equations

Balance for species *i*

$$\frac{\partial}{\partial t}(\varepsilon C_i) = \nabla \cdot \left(D_i \nabla C_i + z_i \frac{D_i}{RT} F C_i \nabla \phi_e \right) + R_i$$

Charge conservation

$$\nabla \cdot \left(\sum_i z_i F \left(D_i \nabla C_i + z_i \frac{D_i}{RT} F C_i \nabla \phi_e \right) \right) = -a \sum_j i_j$$

Butler-Volmer Equation for reaction *j*

$$M \rightleftharpoons M^+ + e^-$$

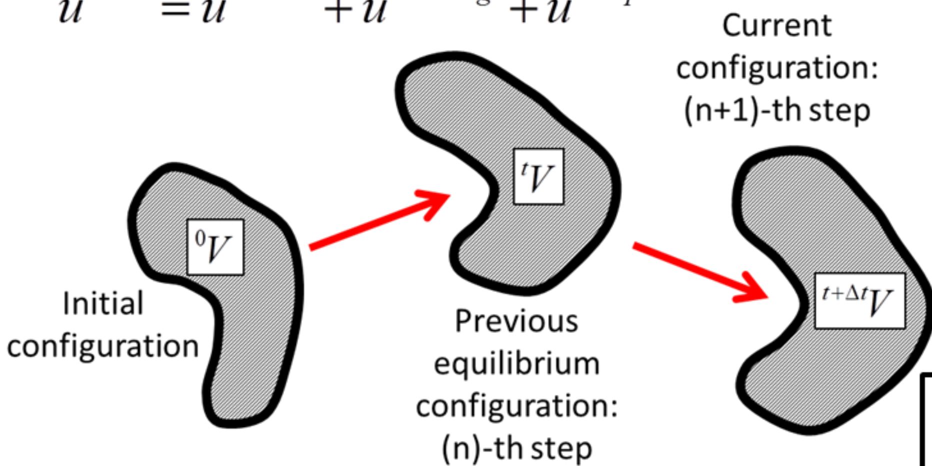
$$i_j = i_j^0 \left\{ \exp\left(\frac{F}{2RT} \eta_j \right) - \left(\frac{C_{M^+}}{C_{M^+}^{ref}} \right) \exp\left(-\frac{F}{2RT} \eta_j \right) \right\}$$

$$\eta_j = \phi_s - \phi_e - U_j$$

C_i	Concentration
D_i	Diffusivity
ϕ_e	Electric potential in electrolyte
R_i	Species generation rate
i_j	Current generation rate due to electrochemical reaction *j*

Details of Poromechanics: Lattice Spring Method

$$u^{total} = u^{elastic} + u^{swelling} + u^{creep}$$



$$\varepsilon^{total} \neq \varepsilon^{elastic} + \varepsilon^{swelling} + \varepsilon^{creep}$$

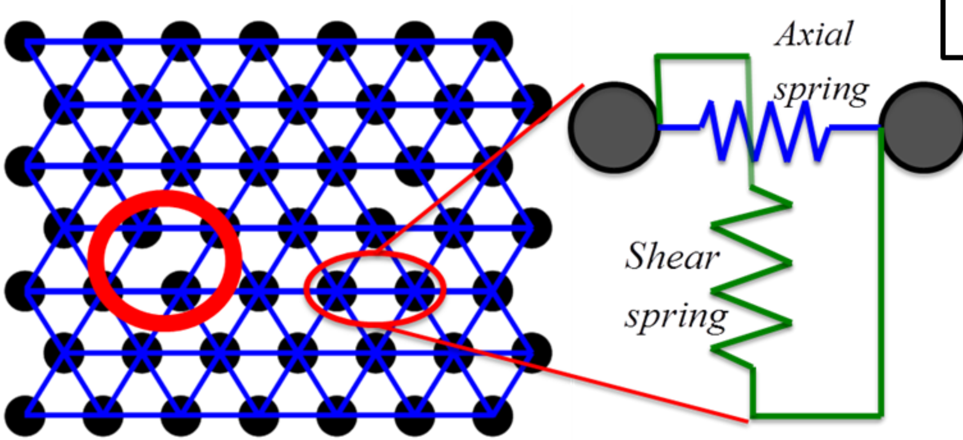
Nonlinear strain-displacement:

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j}\right)$$

Governing differential equation:

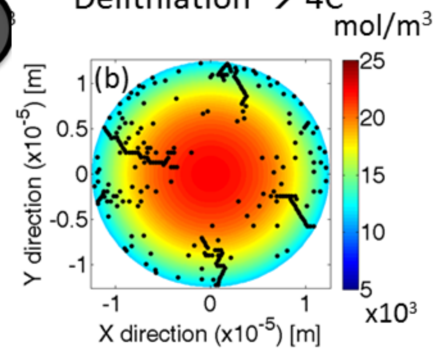
$$\underbrace{\int_{{}^tV} {}^{t+\Delta t}_{\ \ t}S_{ij}\,\delta\,{}^{t+\Delta t}_{\ \ t}\varepsilon_{ij}\,d\,{}^tV}_{\text{Internal energy}} - \underbrace{\int_{{}^tS} {}^{t+\Delta t}_{\ \ t}F_i\,\delta\,{}^{t+\Delta t}_{\ \ t}u_i\,d\,{}^tV}_{\text{External energy}} \approx 0$$

Random Lattice Spring Method

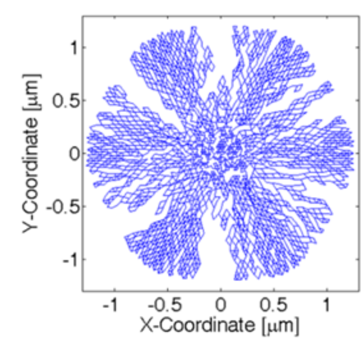


Fracture in Lithium Ion Battery Particles

Delithiation → 4C



High capacity anode materials



Details of Poromechanics: Volume Expansion

$$\frac{d\varepsilon}{dt} = V_{S_{8(s)}} \cdot r_{S_{8(s)}} - V_{Li_2S} \cdot r_{Li_2S} + \boxed{\Delta\varepsilon_{mech}}$$

Effective volume change due to precipitation induced volume expansion.

- External load is the pressure induced by precipitation: $\Delta p_{precip} = \boxed{B_{elec}} \cdot \boxed{\Delta\varepsilon_{precip}}$

Bulk modulus of the electrolyte → **Electrolyte property**

Precipitation induced strain → **Pore confinement effect**

- Precipitation induced strain is given as: $\Delta\varepsilon_{precip} = V_{Li_2S} \cdot \Delta m_{Li_2S} - V_{S_{8(s)}} \cdot \Delta m_{S_{8(s)}}$

$$where, \quad \Delta m_{Li_2S} = 8\Delta m_{S_{8(s)}}$$